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(54) Title: HYDROPHOBIC IONIC SALTS AND NONAQUEOUS ELECTROLYTES

(57) Abstract: Improved nonaqueous electrolytes for application in electrical storage devices such as electrochemical capacitors or high energy density batteries are disclosed. The electrolytes of the invention contain salts comprising alkyl substituted (wherein at least one alkyl group consists of five or more carbon atoms), cyclic delocalized heterocyclic cations, their perfluoro derivatives, and certain polyatomic anions, preferably inorganic perfluoro anions, these salts either used neat, or dissolved in organic solvents, preferably organic carbonate solvents, or liquid inorganic gases or combinations thereof, at a concentration of greater than 0.5M and preferably greater than 1.0M. Exemplary electrolytes comprise 1-methyl-3-*n*-pentylimidazolium hexafluorophosphate dissolved in a cyclic or acyclic organic carbonate, or methyl formate, or a combination thereof. These salts and these improved electrolytes have useful characteristics such as enhanced oxidative stability, wider liquid range, a wider electrochemical window, and high energy storage capabilities and power characteristics compared to prior art electrolytes. Electrochemical double layer capacitors using electrolytes of this invention permit high energy storage at high voltages.

TITLE OF THE INVENTION
HYDROPHOBIC IONIC SALTS AND NONAQUEOUS ELECTROLYTES

5

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the priority of U.S. Provisional Application No. 60/141,956 filed July 1, 1999 entitled, HYDROPHOBIC IONIC SALTS AND NONAQUEOUS
10 ELECTROLYTES FOR ELECTRICAL STORAGE DEVICES, the whole of which is hereby incorporated by reference herein.

STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT

15 Part of the work leading to this invention was carried out with United States government support provided under Contract No. F602-96ER82149 from the Department of Energy. Therefore the U.S. government has certain rights in this invention.

20

BACKGROUND OF THE INVENTION

Significant effort has been invested over the years in improving the energy and power of electrical energy storage devices such as capacitors and batteries. These are
25 particularly useful in short term, high energy applications such as electric vehicles or cellular communication. Warren et al., U.S. Pat. No. 5,418,682, discloses a capacitor having an electrolyte consisting of tetraalkyammonium salts which include nitrile or dinitrile
30 solvent and teaches that such a system provides a high dielectric constant, which is needed for capacitance. Morimoto et al., Pat. No. 4,725,926, discloses a nonaqueous electrolyte comprising quaternary phosphonium salts in

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organic solvents for use in electric double layer capacitors.

A wide variety of solvents and salts are available for such use, offering specific advantages depending on the application being considered (e.g., low temperature vs. high temperature). Certain ionic liquids based on the imidazolium cation have recently received attention as nonaqueous electrolytes in various electrochemical devices (Koch et al., J. Electrochem. Soc. 143:155, 1996). These electrolytes have significant advantages compared to the numerous quaternary onium salts that have been previously investigated for use in carbon double-layer capacitor electrolytes (Ue et al., J. Electrochem. Soc. 141:2989, 1994).

Electrochemical capacitors based on nonaqueous electrolytes offer greater electrochemical stability (up to 4V) compared to aqueous systems, thereby providing greater energy storage ($E = \frac{1}{2}CV^2$). However, due to the lower conductivity of nonaqueous electrolytes compared to aqueous systems, lower power capabilities are observed. In addition, with the porous materials used in electrochemical capacitors, the high viscosity typically associated with the high dielectric constant solvents used in nonaqueous electrolytes is detrimental to conductivity in porous electrodes. Furthermore, the lower ion concentrations typically obtained with prior art nonaqueous electrolytes result in increased electrolyte volume requirements for packaged devices. It is an object of the present invention to solve the above mentioned problems inherent in the use of conventional nonaqueous electrolytes.

BRIEF SUMMARY OF THE INVENTION

In one embodiment, the invention is directed to hydrophobic ionic salts having improved properties for application in non-aqueous batteries, electrochemical
5 capacitors, electroplating, catalysis, lubrication and chemical separations. The hydrophobic ionic salts of the invention consist of C_5 (or greater) alkyl substituted, cyclic delocalized aromatic cations, and their perfluoro derivatives, and polyatomic anions, wherein the appropriate
10 anions exclude those that are both conjugate bases to Lewis acids and have the capability of reacting with moisture to liberate a gaseous product. Furthermore, the anions have van der Waals volumes exceeding 100 \AA^3 .

The ionic salts of the invention possess a wide
15 liquidus range, manifest high thermochemical and electrochemical stability, and are hydrophobic in nature. When the cation and/or the anion is fluorinated, the hydrophobic ionic salts have certain special properties including resistance to extremes of temperature and
20 pressure, resistance to corrosive acids and bases, and inertness to organic solvents and oxidizing agents, making them particularly useful as superior hydraulic fluids and inert liquid diluents for highly reactive chemicals.

Specifically, it has been determined that by simply
25 increasing the number of carbon atoms from four to five (or more) on a sidechain attached to a cationic delocalized heterocyclic ring, one can obtain physical and electrochemical properties for the resultant salts that are strikingly different from prior art. For example, ionic
30 salts with a sidechain of from one to four carbon atoms always reveal a melting point. However, if one simply adds

one or more additional carbon atoms to this side chain, no melting point data may be obtained. That is to say, these new materials undergo only a transition from a liquid to a glass, and, as such, manifest a much wider liquidus range
5 than their four or fewer carbon sidechain homologues.

The oxidative stability of these new materials is also enhanced as one elaborates on the sidechain with additional carbon atoms. On going from a four carbon sidechain to a five (or greater) carbon atoms, a gain of up to 500mV of
10 oxidative stability is obtained. This is a significant benefit which enables the new ionic salts to be employed as electrolytes in high voltage batteries and capacitors.

In another embodiment, which has similar advantages to
15 those described above, the invention is directed to nonaqueous electrolytes containing salts consisting of C_5 (or greater) alkyl substituted, cyclic delocalized aromatic cations, and their perfluoro derivatives, and certain polyatomic anions having a van der Waals volume less than
20 or equal to 100 \AA^3 , preferably inorganic perfluoride anions and most preferably PF_6^- , which are dissolved in organic liquids, preferably alkyl carbonate solvents, or liquid sulfur dioxide or combinations thereof, at a concentration of greater than 0.5M and preferably greater than 1.0M.

25 The nonaqueous electrolytes of the invention are useful in electrical energy storage devices, particularly electrochemical capacitors and high energy density batteries. These electrolytes can also be used in potentiometric and voltametric electrochemical sensors,
30 photovoltaic devices and fuel cells. Further, the electrolytes of the invention will find use as media for

either biphasic or homogeneous catalysis or electrocatalysis.

5 BRIEF DESCRIPTION OF THE DRAWINGS

Other features and advantages of the invention will be apparent from the following detailed description of the invention, taken in conjunction with the accompanying drawings in which:

10 Fig. 1 shows melting points and glass transitions of C₅ MIPF₆/DMEIIm mixed salts;

Fig. 2 shows comparison of the performance of salts of the invention with salts having heterocyclic delocalized cations with shorter length alkyl side chains as
15 electrolytes in an electrochemical capacitor at higher temperatures;

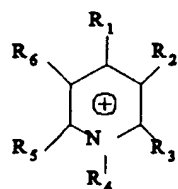
Fig. 3 shows an arrangement of components of an electrochemical cell or battery using a hydrophobic ionic salt or nonaqueous electrolyte of the invention; and

20 Fig. 4 shows an arrangement of components of a capacitor using a hydrophobic ionic salt or nonaqueous electrolyte of the invention.

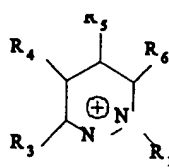
25 DETAILED DESCRIPTION OF THE INVENTION

The hydrophobic ionic salts of the invention include a cation selected from the group consisting of:

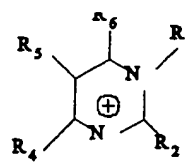
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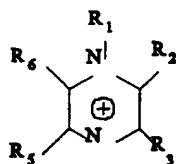
Pyridinium



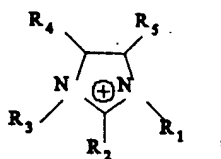
Pyridazinium



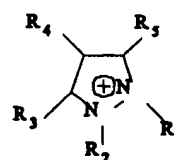
Pyrimidininium



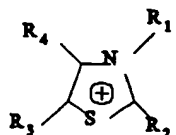
Pyrazinium



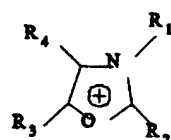
Imidazolium



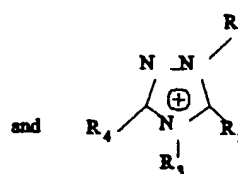
Pyrazolium



Thiazolium



Oxazolium



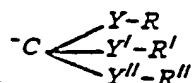
Triazolium

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are either H, F, or separate alkyl groups, respectively, wherein at least one
 5 alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_6$ can be joined together to constitute a unitary alkylene radical forming one or more ring structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may
 10 be substituted with electron withdrawing groups, preferably F-, Cl-, CF_3 -, SF_5 -, CF_3S -, $(CF_3)_2CHS$ - or $(CF_3)_3CS$ -; and a polyatomic anion having a van der Waals volume exceeding 100 \AA^3 , wherein said anion excludes those that are both conjugate bases to Lewis acids and have the capability of

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reacting with moisture to liberate a gaseous product. Preferably, the van der Waals volume of the polyatomic anion exceeds 140 Å³.

An exemplary anion in the hydrophobic ionic salt of the invention is of the following form:

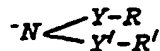


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wherein each of the moieties Y, Y', and Y'', are -SO₂- or -CO-; the groups R and R' are separate halogenated alkyl groups of 1-4 carbon atoms, respectively or are joined together to constitute a unitary halogenated alkylene radical of from 2-4 carbon atoms linking Y and Y' and forming a ring structure which includes R, R', Y, Y', and the carbon atom to which Y and Y' are attached; and the group R'' is an alkyl or haloalkyl radical of 1-4 carbon atoms or a halogenated phenyl group.

In another exemplary anion, the -Y'-R' group in the formula above is replaced by Z, which is an electron-withdrawing substituent selected from the group consisting of -C(O)H, -NO₂, -CN, -F, and perfluorinated alkyls and aryls containing no more than 8 carbons.

A further exemplary anion has the formula:



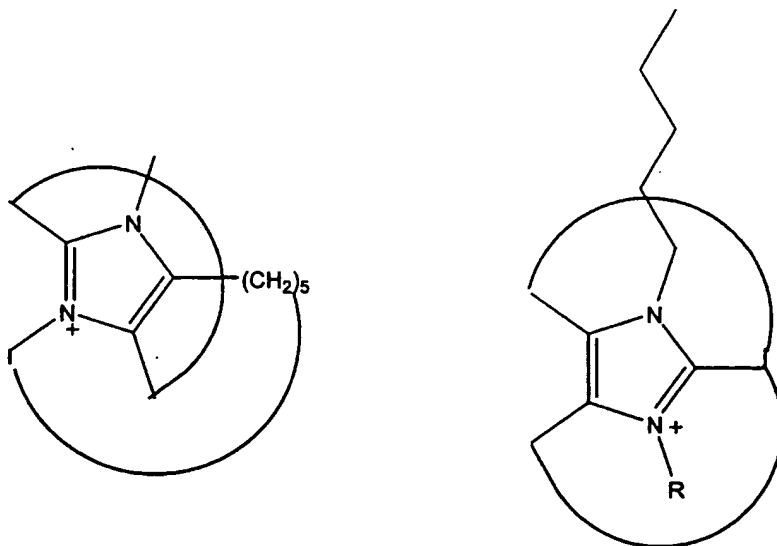
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wherein each of the moieties Y and Y' are -SO₂- or -CO-; and the groups R and R' are separate halogenated alkyl groups of 1-4 carbon atoms.

In the exemplary anions described above, the moieties Y, Y', and Y'' are preferably $-\text{SO}_2-$ moieties. The groups R, R', and R'' each preferably contains one or two carbon atoms. These groups are preferably halogenated with fluorine or chlorine, the most preferred halogen being fluorine, and are preferably perhalogenated. Specific examples include the bis(trifluoromethylsulfonyl)imide $[\text{C}_2\text{F}_6\text{S}_2\text{O}_4\text{N}]$ (Im-) and bis(perfluoroethylsulfonyl)imide $[\text{C}_4\text{F}_{10}\text{S}_2\text{O}_4\text{N}]$ (Beti-) anions.

In other embodiments, the anion is a mono- or di-perfluorosulfonate, or the anion is any one of $(\text{CF}_3)_2\text{PF}_4$, $(\text{CF}_3)_3\text{PF}_3^-$, $(\text{CF}_3)_4\text{PF}_2^-$, $(\text{CF}_3)_5\text{PF}^-$, $(\text{CF}_3)_6\text{P}^-$, $\text{SF}_5\text{CF}_2\text{SO}_3^-$, $\text{SF}_5\text{CHFCH}_2\text{SO}_3^-$, $\text{CF}_3\text{CF}_2(\text{CF}_3)_2\text{CO}^-$, $(\text{CF}_3\text{SO}_2)_2\text{CH}^-$, $(\text{SF}_5)_3\text{C}^-$ or $[\text{O}(\text{CF}_3)_2\text{C}_2(\text{CF}_3)_2\text{O}]_2\text{PO}^-$.

Exemplary cations are C_5MI^+ ,



15

The salts of the invention, containing heterocyclic delocalized cations with at least one alkyl substituent of five or more carbon atoms, were shown to be more

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electrochemically stable than salts with the equivalent cation having all alkyl side chains of four carbons or less in analyses summarized in Tables 1 and 2 below. These analyses were carried out with neat solutions. In general, the C₅-C₇ salts of any of the core cation structures are commonly viscous liquids, the C₁₂-C₂₀ salts usually form liquid crystals and the salts with alkyl substituent lengths greater than C₂₀ are wax-like.

A Mettler DSC821^e was employed to obtain thermochemical data. Differential scanning calorimetry (DSC) data were obtained in a sealed aluminum pan (prepared in a dry box) with a cooling and heating rate of 10 °C/min.

Table 1 presents the results of a DSC experiment run on a set of salts based on the smaller C₂ and C₄ cations (the ethylmethylimidazolium (EMI cation), and the *n*-butylmethylimidazolium (C₄MI cation)) and a set of salts of the invention based on the larger C₅, C₆, and C₇ cations (the *n*-pentyl, *n*-hexyl, and *n*-heptyl methylimidazolium cations (C₅MI, C₆MI, and C₇MI cations, respectively)).

20

Salt	T _g (°C)	T _{mp} (°C)
C ₂ MI Cl	-75	--
C ₂ MI PF ₆	-75	--
C ₅ MI Im	-85	--
C ₆ MI Im	-85	--
C ₇ MI Im	-85	--
C ₅ MI Me	-64	--
EMI PF ₆	--	62
EMI Im	--	-15
C ₄ MI Im	-86	-2
EMI Beti	--	-1
EMI Me	-64	39

It is seen that all salts with the C₅MI or larger cation reveal only glass transition temperatures while all salts with the C₂ and C₄ cations reveal a melting point and, in two cases, both a glass transition temperature and a melting point. These data indicate that salts based on the C₅ and larger cations are fluid to extremely low temperatures where they form a glass, typically in the region from from -75 to -85 °C. Electrolyte fluidity (and therefore good ionic conductivity) at low temperatures, as manifested by the C₅ and larger cations, is critically important for all power source applications and is a highly desirable property. Moreover, an extremely wide temperature range is also important for new solvents where the broad kinetic control of chemical reactions run in such solvents is highly desirable.

This result is quite surprising because each of the C₅ and larger salts possesses a higher molecular weight due to the additional three to five methylene groups compared to the corresponding salts with the C₂ and C₄ cations. Chemical compounds of a homologous series typically manifest higher melting points as the molecular weight increases. This is readily apparent when one compares the melting points of EMIIIm and C₄MIIm. Here the melting point increases from -15 to -2 °C as the molecular weight increases with the addition of two methylene groups. Thus, one skilled in the art would predict that the next salt in this homologous series, i.e., the C₅MIIm would manifest a melting point higher than -2 °C. Yet no melting point whatsoever can be measured. This indicates that there is a

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clear and dramatic break in the physical behavior of these salts when the sidechain is increased from four to five (or more) carbon atoms.

Cyclic voltammetry data were obtained with a freshly polished glassy carbon disk working electrode (0.077 cm²) and a high surface area (26 m²) carbon counter electrode. An EG&G PAR 273A potentiostat/galvanostat was used to obtain cyclic voltammetric data. A silver (Ag) wire was used as a quasi-reference electrode, poised at approximately 3 V vs. Li/Li⁺.

Table 2 presents the results of a cyclic voltammetry experiment run on a set of salts ranging from a C₂ up to a C₆ sidechain on the heterocyclic cation.

15

Table 2. Cyclic Voltammetry Data for Neat Ionic Liquids at 23°C

Electrolyte	Reduction (V)	Oxidation (V)	ΔV
C ₃ MIPF ₆	-2.0	2.2	4.2
C ₃ MIIIm	-2.1	2.1	4.2
C ₆ MIIIm	-2.1	2.5	4.6
C ₃ MIBeti	-2.0	2.4	4.4
C ₃ MIMe	-2.1	2.3	4.4
EMIPF ₆	(Solid at room temperature)		
EMIIIm	-2.0	2.1	4.1
C ₄ MIIIm	-2.0	2.1	4.1
EMIBeti	-2.0	2.1	4.1
EMIMe	-1.9	2.2	4.1

This table shows that all salts comprising a C₅ or larger sidechain provide for a wider electrochemical window than their smaller C₂ and C₄ counterparts. This finding is extremely useful in that the salts based on the larger cations are demonstrably more resistant to chemical and electrochemical oxidation. For example, an electrochemical capacitor employing an electrolyte comprising salts with a C₅ or longer sidechain could be charged to a higher

potential. Since the energy stored by a capacitor is directly proportional to the square of the voltage, a modest increase in the electrochemical voltage window results in a significant increase in the amount of energy stored in an electrochemical double layer capacitor. For non-electrochemical applications, resistance to oxidation is a highly desirable property for ionic salts used as solvents under extreme conditions.

This result is surprising since the extension of an alkyl side chain on the imidazolium ring from two to five carbon atoms is not expected to inductively affect the molecular orbital of the ring. This is because the imidazolium ring does not "see" the additional three methylene groups. The first two carbon atoms comprising the five carbon chain effectively insulate the ring from any electronic affect manifested by the pendent three carbon chain.

Mixture of salts of the invention, containing heterocyclic delocalized cations having long chain substituent alkyl groups, with salts with heterocyclic delocalized cations having alkyl substituent chains of four or fewer carbon atoms have the advantage of possessing good conductivity and of having gel-like qualities. The anions in the mixture of two or more salts may be the same or different. Referring to Fig. 1, it can be seen that mixtures of these salts display additional primary phase transitions indicating liquid crystal behavior in the shaded region. Additionally, the liquid crystal behavior may also be expressed by a variety of mixture types, e.g., mixtures containing one cation and two or more anions, one

anion and two or more cations or two and more cations or anions, may be used.

Fig. 2 presents a Ragone plot of energy density vs. power density for a group of electrochemical double layer capacitors containing either a C₂ or a C₅ ionic liquid electrolyte at two different temperatures. The data reveal that, even though the viscosity of the C₅MIIm is essentially double that of EMIIIm (55 cP vs. 28 cP), the overall performance of the capacitors containing the two different electrolytes is essentially equivalent. One skilled in the art would expect that such a significant increase in electrolyte viscosity on going from the C₂ to the C₅ cation would be extremely detrimental to the amount of energy extractable from the power source.

The benefit provided by the increased viscosity of ionic liquids comprising the C₅ (and larger) heterocyclic cations is one of safety. The more viscous the electrolyte, the less prone to leakage in the event that the seal of the device is compromised.

When the cation and/or the anion is fluorinated, the hydrophobic ionic salts of the invention have certain additional special properties including resistance to extremes of temperature and pressure, resistance to corrosive acids and bases, and inertness to organic solvents and oxidizing agents in analogy with the physical and chemical properties of Teflon®, a solid perfluorinated hydrocarbon, (see, e.g., R.D. Chambers in "Fluorine in Organic Chemistry," Wiley-Interscience, New York, 1973, and references therein). Perfluorinated hydrophobic ionic salts of the invention have applications as superior hydraulic fluids and lubricants, inert liquid diluents for

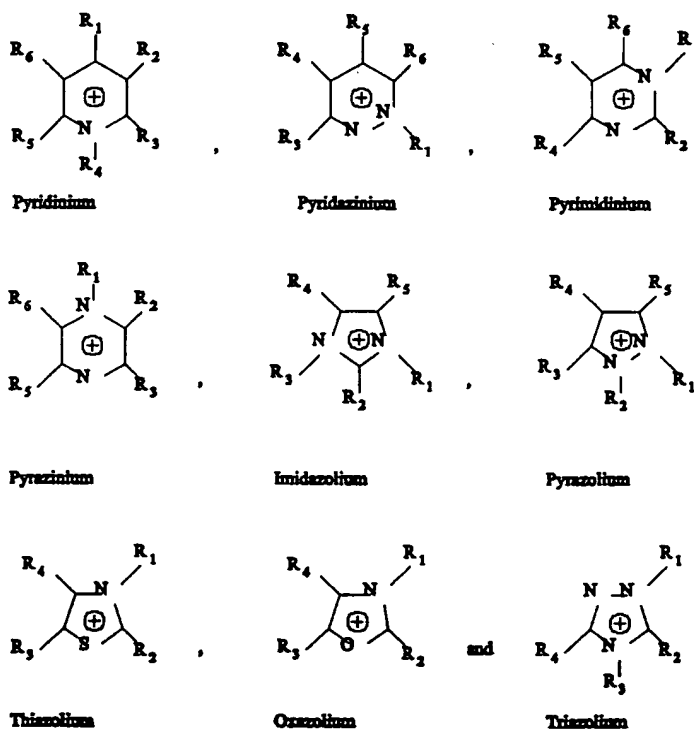
highly reactive chemicals and solvents with a high capacity for dissolved gases such as oxygen, and are useful for catalysis and for oil and gas separations where the desired product is partitioned between an aqueous and hydrophobic
5 perfluorinated ionic liquid phase.

A further advantage of the hydrophobic ionic salts of the invention is their ability to dissolve quantities of alkali and alkaline earth metals, for example, salts such as LiX, NaX, KX, MgX_2 , CaX_2 and AlX_3 (where X = any anion of
10 the invention). The presence of these cations then allows these media to be used as electrolytes in either primary or secondary (rechargeable) high energy density batteries.

Hydrophobic ionic salts of the invention having both large cations and large anions have reduced ionic
15 conductivity. However, the addition of an organic liquid, preferably a polar organic liquid, as a cosolvent enhances the ionic conductivity by lowering the solution viscosity. An improved electrolyte of the invention, for use in an electrochemical cell, includes a hydrophobic ionic salt as
20 described above and an organic liquid, which, in one embodiment, is selected from the group consisting of linear ethers, cyclic ethers, esters, carbonates, lactones, nitriles, amides, sulfones and sulfolanes. In another embodiment, the polar organic liquid is selected from the
25 group consisting of diethylether, dimethoxyethane, tetrahydrofuran, dioxane, dioxolane, methyltetrahydrofuran, methyl formate, ethyl formate, methyl propionate, propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, dibutyl carbonate,
30 butyrolactones, acetonitrile, benzonitrile, nitromethane, nitrobenzene, dimethylformamide, N-methylpyrrolidone,

dimethylsulfone, tetramethylene sulfone, sulfolane and thiophene.

In another embodiment, the invention is directed to a
 5 nonaqueous electrolyte for an electrical storage device,
 the electrolyte including a salt consisting of a cation
 selected from the group consisting of:



10

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are either H, F, or
 separate alkyl groups, respectively, wherein at least one
 alkyl group of 5 or more carbon atoms is present; or any
 two of R_1 - R_6 can be joined together to constitute a
 15 unitary alkylene radical forming one or more ring

structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups, alkylene radicals or phenyl groups may be substituted with electron withdrawing groups; and a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a van der Waals volume $\leq 100 \text{ \AA}^3$, the salt being dissolved at a concentration of greater than 0.5 M in an organic liquid. Preferably, the cation is 1-pentyl-2,3-dimethyl imidazolium or 1-hexyl-2,3-dimethyl imidazolium and the anion is AsF_6^- , BF_4^- , triflate or, most preferably, PF_6^- . Any of the other cations disclosed above as useful in hydrophobic ionic salts of the invention with anions having a van der Waals volume greater than 100 \AA^3 are also useful in this embodiment, with anions having a volume less or equal to 100 \AA^3 . The organic liquid is preferably a linear ether, cyclic ether, ester, carbonate, formate, lactone, nitrile, amide, sulfone or sulfolane, and, most preferably, either a cyclic or acyclic alkyl carbonate or methyl formate. Liquid sulfur dioxide or a mixture of sulfur dioxide and an organic liquid are particularly useful in electrolytes of the invention suitable for low temperature use. The addition of other low viscosity agents, which may include gasses (e.g., CO_2 , NO_2 , N_2O , etc.), may also be used to improve performance, especially at lower temperatures. The electrolyte of the invention may further include, e.g., tetraalkylammonium or tetraalkylphosphonium salt in order to manifest desirable physical or chemical properties preferred by those of skill in the art.

An electrochemical cell or high energy density battery of the invention includes as an electrolyte a hydrophobic ionic salt or nonaqueous electrolyte of the invention.

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Referring to Fig. 3, such a cell 12 has, within a conductive container 14 and cover 15, an anode 16 and a cathode particle mix 18. A separator 20 which includes an electrolyte is placed between the anode and the mix.

5 Container 14 is crimped at the edges 24, capturing cover 15 under an insulating gasket 22. Cells so formed may be configured for either parallel or series operation.

An electrochemical capacitor of the invention similarly includes a hydrophobic ionic salt or nonaqueous electrolyte of the invention and is configured as is shown

10 in Fig. 4. An electrochemical capacitor is an electrochemical storage device in which electric charge is stored in the electrical double-layer formed at the interface between a polarizable electrode and an

15 electrolyte solution when dc voltage is applied. Referring to Fig. 4, such a capacitor 32 has, within a conductive container 34 and cover 35, two electrodes 36 and 38 which may be composed of the same material or different materials. A separator 420 which includes an electrolyte

20 is placed between the two electrodes. Container 34 is crimped at the edges 44, capturing cover 35 under an insulating gasket 42. Capacitors so formed may be configured for either parallel or series operation.

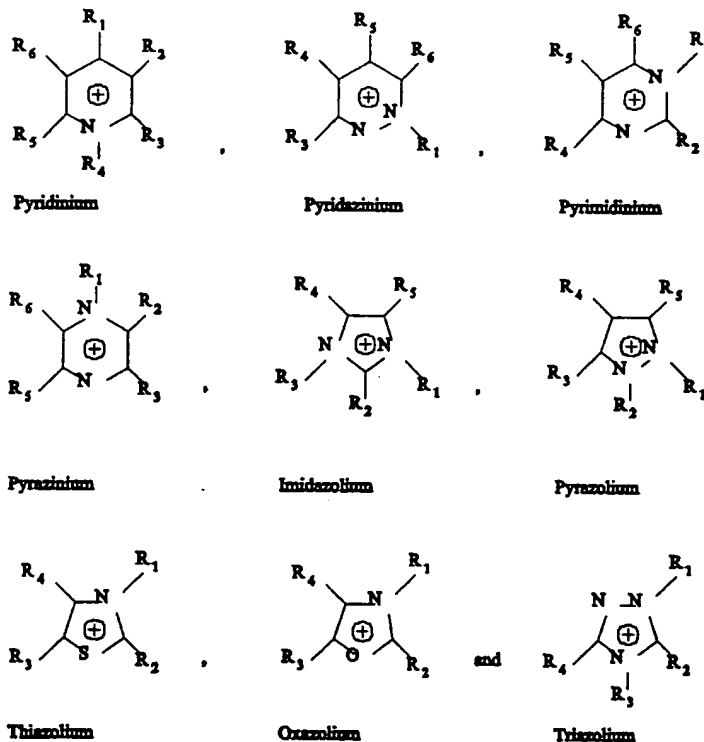
-18-

While the present invention has been described in conjunction with a preferred embodiment, one of ordinary skill, after reading the foregoing specification, will be able to effect various changes, substitutions of
5 equivalents, and other alterations to the compositions and methods set forth herein. It is therefore intended that the protection granted by Letters Patent hereon be limited only by the definitions contained in the appended claims and equivalents thereof.

CLAIMS

1. A ionic salt comprising a cation and an anion, wherein said cation is selected from the group consisting of:

5



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are either H, F, or
 separate alkyl groups, respectively, wherein at least one
 10 alkyl group of 5 or more carbon atoms is present; or any
 two of $R_1 - R_6$ can be joined together to constitute a
 unitary alkylene radical forming one or more ring
 structures converging on the cyclic delocalized aromatic
 ring; and wherein the alkyl groups or alkylene radicals may
 15 be substituted with electron withdrawing groups; and

-20-

wherein said anion is a polyatomic anion having a van der Waals volume exceeding 100 \AA^3 , and wherein further said anion excludes those that are both conjugate bases to Lewis acids and have the capability of reacting with moisture to
5 liberate a gaseous product.

2. The ionic salt of claim 1 wherein, in said cation, a substituent electron withdrawing group is selected from the group consisting of F- , Cl- , $\text{CF}_3\text{-}$, $\text{SF}_5\text{-}$, $\text{CF}_3\text{S-}$, $(\text{CF}_3)_2\text{CHS-}$
10 and $(\text{CF}_3)_3\text{CS-}$.

3. The ionic salt of claim 1 wherein said anion is a mono- or di-perfluorosulfonate.

15 4. An electrolyte for use in an electrochemical cell comprising
the ionic salt of claim 1; and
a polar organic liquid.

20 5. An electrochemical cell comprising
an anode;
a cathode; and
an electrolyte comprising the ionic liquid of claim 1.

25 6. An electrochemical cell comprising
an anode;
a cathode; and
an electrolyte comprising the ionic salt of claim 1
and an alkali or alkaline earth metal.

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7. The electrochemical cell of claim 5 or claim 6, wherein said electrolyte further comprises an organic liquid.

5 8. A capacitor comprising
a first electrode;
a second electrode; and
an electrolyte, said electrolyte comprising the ionic
salt of claim 1.

10

9. A mixture comprising two or more ionic salts of claim 1, said salts comprising first and second cations, wherein, in at least one first cation, at least one of R_1-R_6 is ≤ 4 carbon atoms and, in at least one second cation, at least
15 one of R_1-R_6 is ≥ 5 carbon atoms.

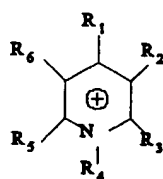
10. The mixture of claim 9 comprising only one kind of anion in said salts.

20 11. The ionic salt of claim 1, wherein two or more different anions are present in said salt.

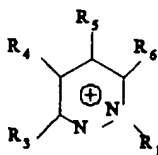
12. A nonaqueous electrolyte for an electrical storage device comprising

25 a salt comprising:
a cation selected from the group consisting of:

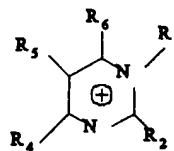
-22-



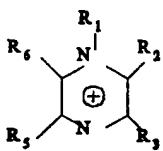
Pyridinium



Pyridazinium



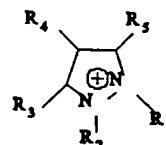
Pyrimidinium



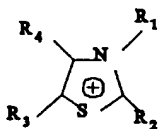
Pyrazinium



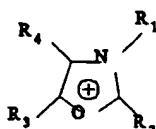
Imidazolium



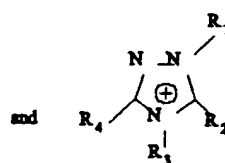
Pyrazolium



Thiazolium



Oxazolium



Triazolium

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are either H, F, or separate alkyl groups, respectively, wherein at least one alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_6$ can be joined together to constitute a unitary alkylene radical forming one or more ring structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may be substituted with electron withdrawing groups; and

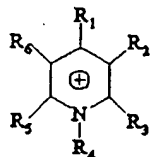
10 a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a Van der Waals volume less than or equal to 100 \AA^3 ,

said salt being dissolved at a concentration of greater than 0.5M in an organic liquid.

13. A nonaqueous electrolyte for an electrical storage device comprising

a salt comprising

5 a cation having the formula



10 wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are either H, F, or separate alkyl groups, respectively, wherein at least one alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_6$ can be joined together to constitute a unitary alkylene radical forming one or more ring structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may be substituted with electron withdrawing groups; and

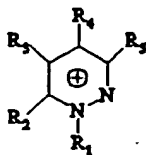
15 a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a Van der Waals volume less than or equal to 100 \AA^3 ,

20 said salt being dissolved at a concentration of greater than 0.5M in an organic liquid.

14. A nonaqueous electrolyte for an electrical storage device comprising

a salt comprising:

a cation having the formula



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wherein R_1 , R_2 , R_3 , R_4 and R_5 are either H, F, or separate alkyl groups, respectively, wherein at least one alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_5$ can be joined together to constitute a unitary alkylene radical forming one or more ring structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may be substituted with electron withdrawing groups; and

a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a Van der Waals volume less than or equal to 100 \AA^3 ,

said salt being dissolved at a concentration of greater than 0.5M in an organic liquid.

15 15. A nonaqueous electrolyte for an electrical storage device comprising

a salt comprising:

a cation having the formula



wherein R_1 , R_2 , R_3 , R_4 and R_5 are either H, F, or separate alkyl groups, respectively, wherein at least one alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_5$ can be joined together to constitute a unitary alkylene radical forming one or more ring structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may be substituted with electron withdrawing groups; and

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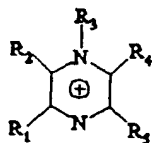
a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a Van der Waals volume less than or equal to 100 \AA^3 ,

said salt being dissolved at a concentration of
5 greater than 0.5M in an organic liquid.

16. A nonaqueous electrolyte for an electrical storage device comprising

a salt comprising:

10 a cation having the formula



15 wherein R_1 , R_2 , R_3 , R_4 and R_5 are either H, F, or separate alkyl groups, respectively, wherein at least one alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_5$ can be joined together to constitute a unitary alkylene radical forming one or more ring
20 structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may be substituted with electron withdrawing groups; and

a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a Van der Waals volume less
25 than or equal to 100 \AA^3 ,

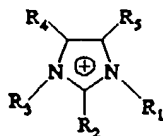
said salt being dissolved at a concentration of greater than 0.5M in an organic liquid.

17. A nonaqueous electrolyte for an electrical storage
30 device comprising

a salt comprising:

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a cation having the formula



5

wherein R_1 , R_2 , R_3 , R_4 and R_5 are either H, F, or separate alkyl groups, respectively, wherein at least one alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_5$ can be joined together to constitute a unitary alkylene radical forming one or more ring structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may be substituted with electron withdrawing groups; and

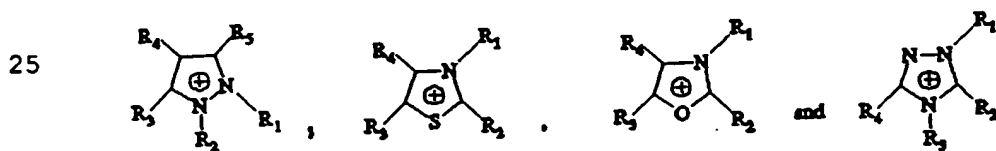
a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a Van der Waals volume less than or equal to 100 \AA^3 ,

said salt being dissolved at a concentration of greater than 0.5M in an organic liquid.

18. A nonaqueous electrolyte for an electrical storage device comprising

a salt comprising:

a cation selected from the group consisting of:



25

wherein R_1 , R_2 , R_3 , R_4 and R_5 are either H, F, or separate alkyl groups, respectively, wherein at least one alkyl group of 5 or more carbon atoms is present; or any two of $R_1 - R_5$ can be joined together to constitute a

30

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unitary alkylene radical forming one or more ring structures converging on the cyclic delocalized aromatic ring; and wherein the alkyl groups or alkylene radicals may be substituted with electron withdrawing groups; and

5 a perfluoro, inorganic anion or a perfluoro, organic sulfonate anion having a Van der Waals volume less than or equal to 100 \AA^3 ,

 said salt being dissolved at a concentration of greater than 0.5M in an organic liquid.

10

19. The electrolyte of claim 12 wherein said organic liquid is selected from the group consisting of linear ethers, cyclic ethers, esters, carbonates, formates, lactones, nitriles, amides, sulfones and sulfolanes.

15

20. The electrolyte of claim 12 wherein said salt is dissolved in liquid sulfur dioxide.

21. The electrolyte of claim 12 wherein said salt is
20 dissolved in a combination of an organic liquid and a low viscosity additive selected from the group consisting of sulfur dioxide, carbon dioxide, nitrogen dioxide, nitrous oxide and other stable inert gases.

25 22. The electrolyte of claim 12 wherein the organic liquid is a cyclic carbonate, an acyclic carbonate, methyl formate or a combination thereof.

23. The electrolyte of claim 12 wherein said salt is
30 dissolved in said organic liquid at a concentration of greater than 2M.

24. The electrolyte of claim 12 wherein said salt is dissolved in said organic liquid at a concentration of greater than 3M.

5

25. An electrical storage device comprising the electrolyte of claim 12.

26. An electrochemical capacitor comprising the
10 electrolyte of claim 12.

27. The electrolyte of claim 12 further comprising a salt consisting of a cation selected from the group consisting of:

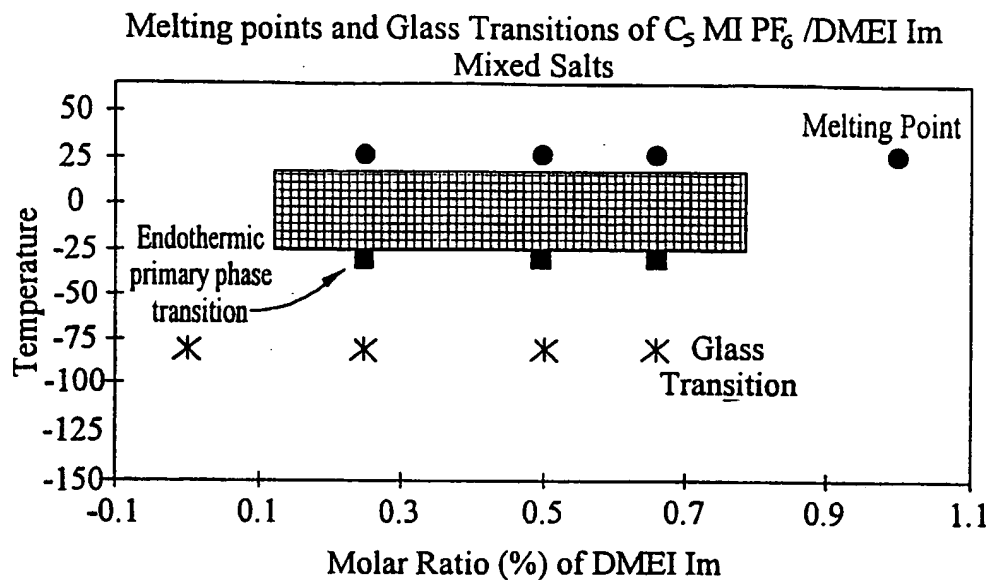
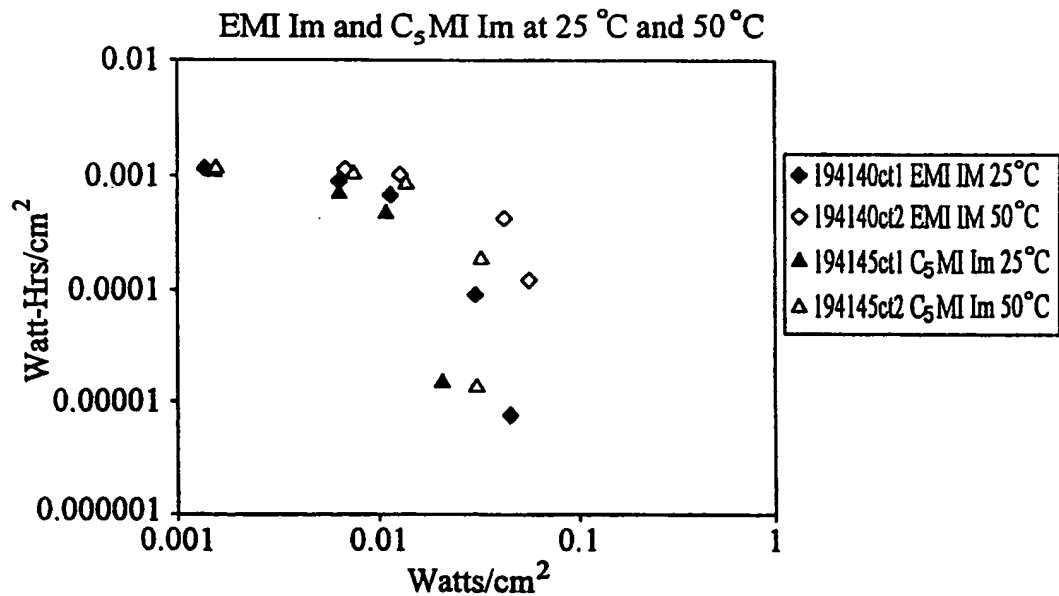


15

wherein R₁, R₂, R₃ and R₄ are separate alkyl groups of from 1 to 10 carbon atoms, respectively, or are joined together to constitute a unitary alkylene radical of from 2 to 20
20 carbon atoms forming a ring structure converging on N or P, respectively;

and an anion having a van der Waals volume less than or equal to 100 Å³.

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**FIG. 1****FIG. 2**